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Experimental and Theoretical Studies on the Conjugation of the Phosphorus−Carbon Double Bond with a Cyclopropyl Group

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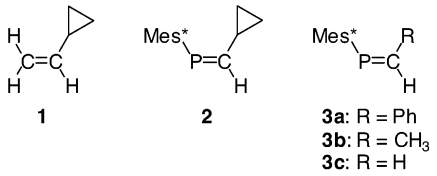
Abstract: X-ray structural analysis for (*Z*)-2-cyclopropyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (**2**) was performed to confirm that the cyclopropyl group largely interacts with the P═C group compared with its carbon analogue, vinylcyclopropane (**1**). Absorption spectrum and redox properties of **2** were also studied to prove the conjugation. Theoretical investigation for nonsubstituted derivatives (**4**) indicated conjugative interaction between the P═C and cyclopropyl groups and revealed the physicochemical similarities between the P═C and C═C bonds.

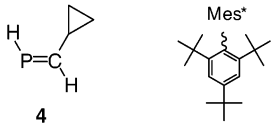
The cyclopropane ring is an organic functional group bearing the smallest ring skeleton; it displays unique properties such as conjugative interaction with π-electron systems.[1] For example, structural elucidation of vinylcyclopropane (**1**) revealed that the cyclopropane ring has a bisected conformation due to the cyclopropyl conjugation with the neighboring C═C group, showing an alternation of two bond lengths in the cyclopropane ring.[2] This conjugation involving the cyclopropyl moiety was established by photoelectron spectrum analysis,[3,4] as well as theoretical investigation.[5] Correspondingly, cyclopropyl conjugations with several unsaturated systems were found[6] and have been used for construction of several extended π-electron systems.[7]

In contrast to hydrocarbon compounds, a number of phosphorus−carbon double-bonded compounds have been synthesized by using the kinetic stabilization method,[8] and we reported various phosphaethenes bearing the 2,4,6-tri-*tert*-butylphenyl (hereafter Mes*) group.[9] The P═C skeleton is nearly apolar as a result of the small difference in the electronegativities of phosphorus and carbon atoms, and it behaves like an alkene, revealing the conjugation with the π-electron systems.[8,10] Recently we reported a 1-phosphaallene [−P═C═C<] bearing a cyclopropylidene group and showed an interaction of the P═C moiety with the three-membered skeleton.[11] Additionally, we described preparation of (*Z*)-2-cyclopropyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (**2**) by γ-elimination with potassium *tert*-butoxide.[11] Compound **2** is a suitable derivative to estimate the conjugation of the P═C and cyclopropyl moieties.

We report here the X-ray crystallography of **2** together with the absorption spectrum and redox properties, indicating considerable interaction of the cyclopropane ring with the P═C moiety. We also describe the results of ab initio calculation to evaluate this cyclopropyl conjugation with the results of other conjugated systems.



1 **2** **3a**: R = Ph **3b**: R = CH_3 **3c**: R = H



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As described in our previous report, **2** was prepared from (*Z*)-5-bromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphapentene and potassium *tert*-butoxide[11] and crystallized from ethanol. A single crystal was employed for X-ray structural determination. Figure 1 displays the molecular structure of **2**, and Table 1 lists the bond lengths and angles. Two independent molecules were assigned in the crystal lattice, and one of them is shown in Figure 1.

The Mes* group is perpendicular to the P═C bond to protect sterically the inherently unstable multiple bond of trivalent phosphorus. The cyclopropane ring is nearly perpendicular to the P−C1−C2 plane, taking the *anti* conformation. The P═C length is very similar to that of 2-phenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (**3a**) [1.674(2) Å][12] The bond lengths of C2−C3 and C2−

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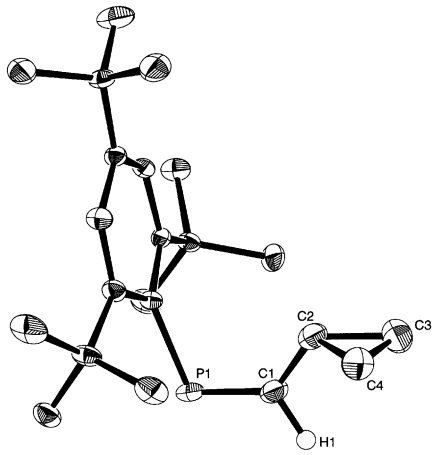
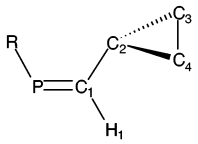


FIGURE 1. ORTEP drawing for one molecule of **2** with 50% probability ellipsoids. Hydrogen atoms other than H1 are omitted for clarity.

TABLE 1. Bond Lengths (Å) and Angles (deg) of 2 and 4



	2[a] (R = Mes*)		**4B**[b] (R = H)
P−C1	1.667(3)	1.664(3)	1.684
C1−C2	1.452(4)	1.456(3)	1.469
C2−C3	1.527(4)	1.522(4)	1.523
C2−C4	1.532(4)	1.529(5)	1.523
C3−C4	1.489(5)	1.489(5)	1.502
Δ1[c]	0.038	0.033	0.021
Δ2[d]	0.043	0.040	0.021
R−P−C1	103.2(1)	103.2(1)	96.2
P−C1−C2	132.3(2)	132.8(3)	129.0
H1−C1−C2	111(1)	111(2)	115.0
C1−C2−C3	118.9(3)	118.7(3)	118.8
C1−C2−C4	117.8(3)	119.2(3)	118.8
C3−C2−C4	58.3(2)	58.4(2)	59.1
C2−C3−C4	61.1(2)	61.0(2)	60.4
C2−C4−C3	60.7(2)	60.6(2)	60.4

[a] X-ray data. [b] MP2/6-311+g(d,p) level. [c] [C2−C3] − [C3−C4]. [d] [C2−C4] − [C3−C4].

C4 are remarkably longer than that of the distal C3−C4 bond. These differences in the bond lengths (Δ1 = [C2−C3] − [C3−C4], Δ2 = [C2−C4] − [C3−C4]) are larger than the corresponding data for **1** (0.015 Å).[2,6] Moreover, the C1−C2 bond is shorter than the corresponding length for **3a** [1.465(3) Å].[12] These results suggest that the interaction of the cyclopropane ring with the P=C system is stronger than that with the C=C group, and the quantity is comparable to the cyclopropyl conjugation with dienyl as observed in spiro[2.4]hepta-4,6-diene.[6] This large conjugation of the cyclopropyl group with the P=C bond might be due to a higher HOMO and a lower LUMO of P=C, compared with its carbon analogue.

In the UV absorption spectrum, **2** revealed a bathochromic shift to **3b**, indicating an extended conjugation and suggesting that the cyclopropyl group is more effectively conjugated with the P=C moiety than the methyl group in **3b** [λ_{max} (log ϵ) 300 (2.9), 240 nm (4.2)].[13] Similar phenomena in UV spectra were observed in some

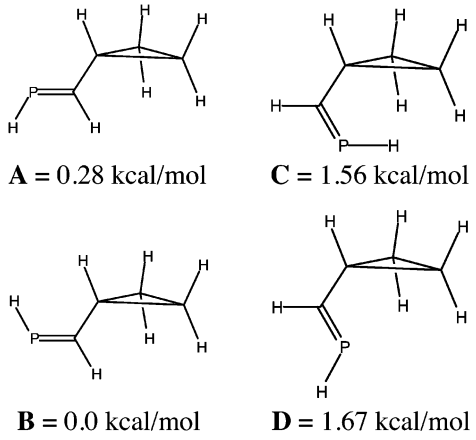


FIGURE 2. Geometric isomers and relative energies of **4**.

cases of hydrocarbon derivatives, such as spiro[2.5]oct-4-ene.[6b] Additionally, we analyzed **2** using cyclic voltammetry to understand the redox potentials of the system. An irreversible oxidation potential E_p^{ox} of 1.68 V and reduction potential E_p^{red} of −0.71 V vs Ag/AgCl (in CH_2Cl_2) were observed. The redox potential data of **2** indicated a higher HOMO as well as a lower LUMO compared with **3c** (E_p^{ox} 1.76 V, E_p^{red} −0.87 V).[14] Thus, these physical data support the considerable conjugation between the P=C and cyclopropyl groups.

We theoretically investigated 2-cyclopropy-1-phosphaethene **4** and the related compounds. Figure 2 displays four different conformations, **4A**−**D**, with the relative energies calculated at the MP2/6-311+g(d,p) level.[15] The exo conformations (**A**, **B**) are more stable than the endo conformations (**C**, **D**). The *Z*-configuration (**B**) is slightly more stable than the *E*-configuration (**A**). Photolysis of (*Z*)-**2** in benzene with a medium-pressure mercury lamp for 3 h afforded a mixture of 3:1 *Z*/*E* isomers. This *Z*-configuration preference in **2** can be ascribed to the CH-π interaction[16] between the neighboring *tert*-butyl protons of the Mes* group and the cyclopropane moiety.

The calculated geometry of the optimized structure of **4** (**B** form) is displayed in Table 1, and the bond lengths of **4B** and its related compounds are summarized in Table 2. The optimized structure, **4B**, is comparable to the observed values in **2**. The conjugation of a C=C double bond with a cyclopropane ring causes similar effects: a C−C bond shortening and a C=X bond elongation with an elongation of the proximal bonds in the cyclopropyl

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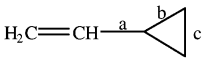
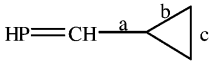
TABLE 2. Optimized Bond Lengths (Å) for 1, 4, and the Related Molecules; Values in Parentheses Are Experimental Data

No.	Molecule	P=C	C=C	C–C
1	$H_3C–CH_3$			1.529 (1.5324)[a]
2	$H_2C=CH_2$		1.339 (1.3327)[b]	
3	$HP=CH_2$	1.674 (1.670)[c]		
4	$HP=CH–CH_3$	1.680		1.503
5	$H_2C=CH–HC=CH_2$		1.347 (1.337)[d]	1.460 (1.483)[d]
6	$HP=CH–HC=CH_2$	1.691	1.350	1.454
7	cyclopropane			1.510 (1.5139)[e]
8	 **1**		1.344 (1.334)[f]	a 1.475 (1.473)[f] b 1.519 (1.514) c 1.505 (1.483)
9	 **4B**	1.684		a 1.469 b 1.523 c 1.502

[a] Reference 17. [b] Reference 18. [c] Reference 19. [d] Reference 20. [e] Reference 21. [f] Reference 22.

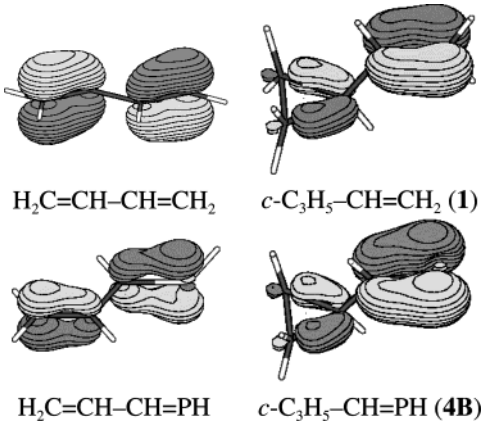


FIGURE 3. Shape of HOMO for **4B** and its related molecules.[21]

group. The shortest C=X (X = C, P) bond is observed in the nonconjugated molecule. Figure 3 shows the shape of the HOMO for **4B** with those for the related species. The butadiene-like structure of the π orbitals and the similarity among them are both clear. The shape of the HOMO for vinylcyclopropane (**1**) is identical to those described in the other reports.[4]

An orbital correlation diagram (see Supporting Information) suggests the similarity in the π-conjugation of 1-phosphabutadiene and *c*-C_3H_5CH=PH (**4B**). The explanation is similar to that for the electronic structure of butadiene. The interaction of the π-orbitals between ethene and phosphaethene results in the huge split between the lowest π1 orbital and the π2 HOMO level. The similar orbital correlation between phosphaethene and the saturated cyclopropane ring is clear. In this case the π-orbital of phosphaethene interacts with the σ ring orbital of appropriate symmetry (a'' symmetry in C_s point group). The correlation diagram also shows the MO correlation of the related carbon compounds, butadiene and **1**. Thus, the similarities in the conjugative ability of the C=C and P=C bonds have been established.[10]

In conclusion, the structure of a stable cyclopropylphosphaethene **2** was unambiguously determined by X-ray crystallography. The cyclopropane ring interacts considerably with the P=C bond and the cyclopropyl conjugation involving the P=C bond is larger than that observed in its carbon analogue, vinylcyclopropane (**1**). The conjugation between the P=C and cyclopropyl groups was explained by the absorption spectra and cyclic voltammetry. Theoretical investigation indicated this cyclopropyl conjugation with the P=C bond and revealed the similarities in P=C and C=C bonds.

Experimental Section

Preparation of 2. A mixture of potassium *tert*-butoxide (1.34 mmol) in THF (10 mL) at 0 °C was added to a solution of (*Z*)-5-bromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene[11] (280 mg, 0.680 mmol) and warmed to room temperature. The reaction mixture was stirred for 30 min, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexane) to afford 132 mg of **2** (45% yield). Data for **2**: colorless crystals, mp 98−99 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 232; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (m, 2H, Mes*), 6.57 (dd, 1H, $^2J_{PH}$ = 38 Hz, $^3J_{HH}$ = 11 Hz, P=CH), 1.59 (s, 18H,

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o-C(CH_3)$_3$), 1.38 (s, 9H, *p*-C(CH_3)$_3$), 0.85 (m, 1H, CH), 0.69 (m, 2H, C*H*H), 0.48 (m, 2H, CH*H*); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 177.7 (d, $^1J_{PC}$ = 43 Hz, P=C), 154.6 (s, *o*-Mes*), 149.9 (s, *p*-Mes*), 137.0 (d, $^1J_{PC}$ = 59 Hz, *ipso*-Mes*), 121.7 (s, *m*-Mes*), 38.5 (s, *o*-*C*(CH_3)$_3$), 35.4 (s, *p*-*C*(CH_3)$_3$), 33.4 (d, $^4J_{PC}$ = 7 Hz, *o*-C(*C*H_3)$_3$), 31.8 (s, *p*-C(*C*H_3)$_3$), 18.3 (d, $^2J_{PC}$ = 21 Hz, CH), 10.6 (d, $^3J_{PC}$ = 7 Hz, CH_2); UV (hexanes) λ_{max} (log ϵ) 300 (sh, 3.5), 254 nm (sh, 4.3); FAB-MS *m*/*z* (rel int) 330 (M^+; 45), 315 ($M^+ - CH_3$; 100). Anal. Calcd for $C_{22}H_{35}P$: C, 79.95; H, 10.67. Found: C, 79.71; H, 10.77.

X-ray Crystallography for 2. $C_{22}H_{35}P$, M = 330.49, triclinic, $P\bar{1}$(No. 2), a = 11.2406(7), b = 20.008(2), c = 9.3703(9) Å, α = 103.125(2)°, β = 90.143(3)°, γ = 89.988(5)°, V = 2052.3(3), Z = 4, T = 120 K, $2\theta_{max}$ = 55.0°, ρ_{calc} = 1.070 g cm^{-3}, μ(Mo Kα) = 0.133 mm^{-1}, 16168 observed reflections, 6267 unique reflections (R_{int} = 0.040), $R1$ = 0.064 ($I > 2\sigma(I)$), $R_W(F)$ = 0.071 (all data), S = 1.50 (695 parameters). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-210342.

Cyclic Voltammetry of 2. Cyclic voltammetry conditions: 1 mM in dichloromethane; supporting electrolyte, 0.1 M tetrabutylammonium perchlorate (TBAP); working electrode, glassy carbon; counter electrode, platinum wire; reference electrode, Ag/AgCl [$E_{1/2}$ (ferrocene/ferricinium) = +0.60 V] at 20 °C; scan rate, 50 mV sec^{-1}.

Photolysis of 2. A solution of (*Z*)-**2** (0.015 mmol) in benzene-d_6 (0.35 mL) was irradiated in a NMR tube with a medium-pressure Hg lamp (100 W) at 5 °C. After irradiation for 3 h, the peaks due to **2** and the isomer (*E*)-**2**[11] were observed in a 3:1 ratio in ^{31}P NMR spectrum. The *Z*/*E* peak ratio did not change even after irradiation for 24 h.

Ab initio Calculation. Calculations were carried out using the Gaussian 98 package[15] with the MP2/6-311+g(d,p) level of theory. The nature of the stationary points was further checked with second derivative calculations to prove that the optimized geometries were real minima on the potential energy surface. To check the reliability of the calculations, several basis sets were tried at the HF, MP2, and QCISD levels. The results of calculations were not sensitive to the basis set but were significantly modified by inclusion of electron correlation. Because the deviation among the results of higher-level calculations was small, we ignored the HF calculations and drew conclusions only from the MP2 results.

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Supporting Information Available: General experimental procedure, UV spectra for **2** and **3b**, cyclic voltammograms for **2**, and Cartesian coordinates and total energies for **4A**−**D**. This material is available free of charge via the Internet at http://pubs.acs.org.

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